

XPS as a Probe of Gap Opening in Many Electron Systems

Robert Haslinger and Nic Shannon

Department of Physics, University of Wisconsin-Madison, 1150 Univ. Av., Madison WI 53706-1390, USA.

(February 1, 2008)

Core hole photoemission (XPS) provides a powerful indirect probe of the low energy excitations of a many electron system. We argue that XPS can be used to study the way in which a gap opens at a metal–superconductor or metal–insulator transition. We consider the “universal” physics of how the loss of low energy excitations modifies XPS spectra in the context of several simple models, considering in particular the case of a two dimensional d-wave superconductor.

PACS nos. 82.80.Pv,74.25.Jb,71.30.+h

I. INTRODUCTION

As a many electron system undergoes a phase transition, the nature of its low energy excitations is usually radically altered. For this reason, experiments which are sensitive to the rearrangement, and in particular to the loss of, low energy excitations (to the opening of a gap), can inform us about how phase transitions take place. Nuclear Magnetic Resonance (NMR) has been used widely in this context to study how low lying *spin* excitations evolve in different phases. Famously, NMR reveals a second “transition” temperature T^* in the underdoped cuprate superconductors, below which a gap opens to spin excitations, even in the absence of superconducting order [1].

In several previous articles [2] [3] one of us proposed the use of core level photoemission (XPS) as a complimentary probe to NMR, offering similar insight into the evolution of *charge* carrying excitations. In the case of the underdoped cuprates, the comparison of XPS and NMR might shed some light on the existence or absence of *spin-charge separation* by answering the question of whether or not a gap opens to charge excitations at the spingap temperature T^* . In fact there are many scenarios in which such a comparison might be informative — for example in metal–insulator transitions where electron–electron interaction is strong.

The opening of a charge gap in a metallic system has certain simple systematic consequences for XPS lineshapes — an overall shift in the core line, and a transfer of spectral weight from high energies to the line threshold. These effects, both due to the suppression of low energy density fluctuations can be understood on quite general physical grounds without recourse to specific models or calculations [4].

In this article, we develop a more quantitative picture of how XPS lineshapes evolve with the opening of a gap by applying perturbation theory to simple models of a metal–semiconductor and metal–superconductor transitions. A good understanding of the behaviour of the simplest models is clearly a necessary first step for the interpretation of experiment in more complicated material examples, such as the cuprates. With this in mind we make a detailed case study of the way in which the familiar asymmetric Doniach–Sunjic lineshape for a core level in a metal [5] is modified by the opening of a superconducting gap in s– and d–wave superconductors, discussing the role of nodes in the gap.

We begin in Section II with an outline of the simple perturbative formalism used to calculate lineshapes and associated shifts. In Section III we calculate the XPS spectrum for a band metal and a simple toy model of a semiconductor within perturbation theory. In Section IV we consider lineshapes and shifts of s– and d–wave superconductors for a free electron gas and a d–wave superconductor on a two dimensional tight binding lattice at half filling.

The qualitative picture for the evolution of the XPS lineshape set out in [4] is found to hold; differences in detail for different models are explored quantitatively. In the concluding Section VI we discuss the consequences and limitations of these results, as applied to experiment, emphasizing the potential role of XPS as a diagnostic tool for strongly correlated systems.

II. FORMALISM

In an XPS experiment a high energy (X–Ray) photon ejects a single electron from a tightly bound atomic level in the sample material, typically a prepared metal surface. The energy distribution of the emitted photoelectrons is measured. Within the sudden approximation, and neglecting all momentum dependence of the matrix elements, the XPS lineshape for the core level is simply proportional to the spectral function for the resulting core hole [6]. Because photoemission leaves behind this unscreened and massive positive charge (recoil of the core hole can safely be neglected) it is accompanied by a violent low energy “shake up” of the remaining itinerant electrons. This manybody effect has important consequences for the core lineshape, as described below, and it is the suppression of the “shake up” by a gap to charge excitations which makes XPS useful as a probe of different phases.

In practice various other mechanisms serve to limit the lifetime of the core hole — which must eventually be filled by the decay of an electron from a higher energy level — and we model these by convoluting the calculated lineshape with a Lorentzian of width the inverse core level lifetime. We neglect a further (temperature dependent) broadening due to phonon processes, which could be accounted for by further convolution with a Gaussian. Perhaps more importantly, we do not consider the case on which the core hole binds an itinerant electron. This leads to the possibility of more than one line

accompanying each core level, which has been treated for the ordinary free electron gas by several authors [7].

We model the combined system of core level and itinerant electrons with the simple Hamiltonian

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{V}_c \quad (1)$$

where \mathcal{H}_0 is the unperturbed Hamiltonian describing the itinerant electron system, and

$$\begin{aligned} \mathcal{V}_c &= \epsilon_d d^\dagger d + V(t) \\ &= \epsilon_d d^\dagger d + \frac{1}{\nu^2} \sum_{k,q} V(q) c_{k-q}^\dagger(t) c_k(t) \end{aligned} \quad (2)$$

switched on suddenly at $t=0$ when the core hole is created. ϵ_d is the energy of the core hole, d is the core hole annihilation operator and c the electron annihilation operator. Spin does not enter into the problem and has been suppressed in our notation.

We model gapless systems as a band of spinless non-interacting electrons

$$\mathcal{H}_0 = \sum_k \epsilon_k c_k^\dagger c_k \quad (3)$$

characterized by a density of states $N(\omega) = \sum_k \delta(\omega - \epsilon_k)$. Semi-conductors are modeled in the same way, but with zero density of states within the gap $|\omega| < \Delta$. We use the usual BCS description of superconducting systems, with quasi-particle dispersion $E_k^2 = \epsilon_k^2 + \Delta_k^2$, where ϵ_k is the underlying band dispersion and Δ_k the (momentum dependant) superconducting order parameter.

Within the sudden approximation [6], the XPS spectrum is proportional to the core electron spectral function

$$A_h(\omega) = -2Im \{ G_h^{ret}(\omega) \} \quad (4)$$

where $G_h^{ret}(\omega)$ is the retarded core hole Green's function. From this definition it follows that the spectral function is normalized to 2π , and spectral weight must always be conserved in XPS lineshapes.

The Green's function for the core hole must be calculated using the full wavefunction for the many electron system *including* the itinerant electrons, and therefore involves matrix elements for the overlap of the many-electron groundstate with all the different states excited by the suddenly switched core hole. In this indirect way XPS probes the spectrum of the itinerant electron liquid.

In the absence of any interaction with the core hole ($V(q) \equiv 0$) the itinerant electrons remain in their ground state and the core hole spectral function is a single coherent delta function peak

$$A_h(\omega) = 2\pi\delta(\omega - \epsilon_d) \quad (5)$$

Interaction with itinerant electrons transfers spectral weight to an incoherent tail and, under certain conditions, eliminates the coherent (delta function) part of the spectral function entirely.

We evaluate $G_h^{ret}(t)$ in the presence of interaction ($V(q) \neq 0$) using a linked cluster expansion [8]

$$G_h^{ret}(t) = -i\theta(t)e^{-i\epsilon_d t} \exp \left[\sum_{l=1}^{\infty} F_l(t) \right] \quad (6)$$

where the coefficients $F_l(t)$ are given by:

$$F_l(t) = \frac{1}{l} (-i)^l \int_0^t dt_1 \dots \int_0^t dt_l \langle |TV(t_1) \dots V(t_l)| \rangle_{connected} \quad (7)$$

The leading term in this series, $F_1(t)$, is purely real and contributes only an absolute shift in the core line. For a purely local interaction ($V(q) = V_0$), this is simply proportional to the density of electrons, and therefore unchanged by the opening of a gap.

It is the second order term, $F_2(t)$, which contains interesting many body physics and, to second order in $V(q)$, determines the XPS lineshape. This is seen to be related to the density-density correlation function (charge susceptibility), and indeed it can be rewritten as:

$$\begin{aligned} F_2(t) &= \frac{1}{\nu} \sum_q |V(q)|^2 \{ \frac{i}{2} \chi'_\rho(q, \omega=0) t \\ &\quad + \frac{1}{\pi} \int_0^\infty d\omega \chi''_\rho(q, \omega) \frac{1 - e^{-i\omega t}}{\omega^2} \} \end{aligned} \quad (8)$$

where χ'_ρ and χ''_ρ are the real and imaginary parts of the retarded density-density correlation function in frequency space [9].

The first part of this expression is an energy shift. It is sensitive to the opening of a gap and for delta function interaction it is proportional to the real part of the local charge susceptibility. The second, more complicated term, determines the line shape. We write this as :

$$\bar{F}_2(t) = - \int_0^\infty R(\omega) \frac{1 - e^{-i\omega t}}{\omega^2} \quad (9)$$

where:

$$R(\omega) = -\frac{1}{\pi} \sum_q |V(q)|^2 \chi''_\rho(q, \omega) \quad (10)$$

is a spectral representation of the perturbation. The core hole—itinerant electron interaction $V(q)$ is short ranged, and for the purposes of this article may be approximated by the purely local interaction $V(q) = V_0$, so

$$R(\omega) = -\frac{1}{\pi} |V_0|^2 \sum_q \chi''_\rho(q, \omega) \quad (11)$$

To find the XPS lineshape within these approximations is then a matter of calculating the imaginary part of the local density-density correlation function as a function of frequency. In the next section we work several examples, re-deriving the familiar asymmetric (Doniach–Sunjic) lineshape for a core level in a metal and showing how it is modified by the opening of a gap in the excitation spectrum.

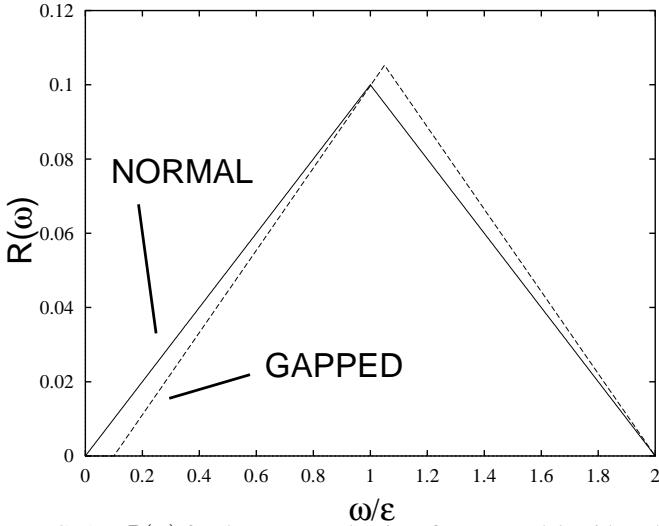


FIG. 1. $R(\omega)$ for the constant density of states model, with and without a gap of $\Delta/\epsilon = 0.05$. The asymmetry exponent is $\alpha = 0.1$.

III. BAND METALS AND SEMI-CONDUCTORS

In this section we will calculate the lineshape for a normal metal, modeled as a band of non-interacting electrons using Eqn. 9, and observe how it changes when a gap is opened in the density of states. For simplicity we assume zero temperature and a delta function potential for the core hole.

Within a non-interacting picture, $R(\omega)$ can be found from the imaginary part of the particle-hole bubble

$$R(\omega) = \frac{|V_0|^2}{\nu^2} \sum_{k,p} [n(\xi_p) - n(\xi_k)] \delta(\omega + \xi_p - \xi_k) \quad (12)$$

We consider a flat density of states centered about the fermi energy, such that :

$$N(\omega) = \begin{cases} N_0 & |\omega| < \epsilon \\ 0 & |\omega| > \epsilon \end{cases} \quad (13)$$

$R(\omega)$ is then easily calculated.

$$R(\omega) = \begin{cases} \alpha\omega & 0 < \omega < \epsilon \\ \alpha(2\epsilon - \omega) & \epsilon < \omega < 2\epsilon \\ 0 & \omega > 2\epsilon \end{cases} \quad (14)$$

where $\alpha = 2N_0^2|V_0|^2$ (the 2 is from the spin summation). In what follows we will use α as a parameter, rather than separately specifying the bare density of states N_0 and the interaction strength V_0 . Since these are unchanged by the opening of a gap, values of α found from experiments on the metallic phase of materials can be used to parameterize predictions for the their XPS lineshapes in a gapped phase. Empirically, $\alpha \sim 0.1$ for most simple metals, and all plots in this paper have been calculated for $\alpha = 0.1$.

On substitution of Eqn. 14 in Eqn. 9 we find that the expected deltafunction at threshold is lost and instead $A(\omega)$ diverges as $\omega^{\alpha-1}$ as $\omega \rightarrow 0_+$. This power law singularity is

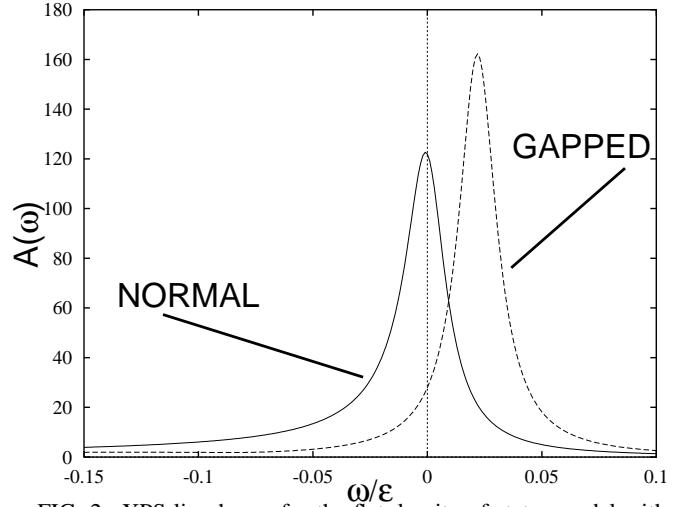


FIG. 2. XPS lineshapes for the flat density of states model with and without a gap of $\Delta/\epsilon = 0.05$. The inverse core hole lifetime is $1/\tau = 0.01\epsilon$, and $\alpha = 0.1$. The opening of a gap causes spectral weight to be shifted out of the powerlaw tail and back into the restored delta function peak. In addition, the entire XPS line shape (delta-function and incoherent tail) undergoes a rigid shift to lower binding energy.

broadened by the core hole lifetime, yielding an asymmetric lineshape essentially equivalent to that calculated by Doniach and Sunjic [5]. The XPS lineshape for this simple band metal formed by numerically convoluting the spectral function with a Lorentzian lifetime envelope is plotted in Fig. 2. We have reversed the energy axis in this and all other plots of lineshapes for ease of comparison with photoemission spectra.

The replacement of the delta function peak in $A_h(\omega)$ with a power law singularity is a consequence of Anderson's *orthogonality catastrophe* [10,12]. The sudden switching of the core hole in the photoemission process leads to the creation of itinerant electron-hole pairs with all possible energies and therefore to a high energy tail in the spectral function. Since the number of electron-hole pairs created with zero energy is logarithmically divergent, the ground states of the perturbed and unperturbed systems are orthogonal, and there is no delta function peak at threshold. The orthogonality catastrophe is effective in a band of non-interacting electrons whenever the density of states at the chemical potential is finite, *i. e.* for any band metal. While all our analysis is limited to second order in the potential \mathcal{V} , this is usually small, and the physics of the orthogonality catastrophe is in any case essentially unaltered by the inclusion of higher order processes (multiple particle-hole excitations) [14].

We now calculate the lineshape for a toy model of a gapped system. The presence of the gap will cut off the number of low energy excitations made by the core hole, eliminating the orthogonality catastrophe. The gap has little effect at higher energies, so away from threshold the lineshape for a system with a small gap should be essentially unchanged. The failure of the orthogonality catastrophe will however lead to the restora-

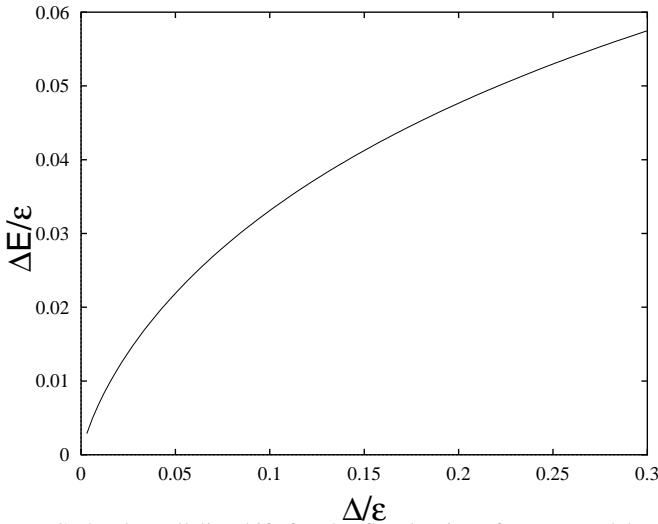


FIG. 3. Overall lineshift for the flat density of states model at various gap magnitudes. This is a shift away from the power law tail, *i.e.* to lower binding energy. ($\alpha = 0.1$).

tion of a delta function peak at threshold. As the gap becomes bigger progressively more spectral weight is transferred to this peak, so that for large gaps the effective lineshape after convolution with a Lorentzian will be the symmetric peak associated with an insulator.

At the same time the overall threshold for the XPS line is shifted to lower energies because the redistribution of charge in the electron gas is suppressed by the opening of the gap, and therefore less work is done inserting a core hole into the system.

If, for sake of illustration, we assume that a gap opens such that the new density of states is :

$$N(\omega) = \begin{cases} N_0 \left(\frac{\epsilon}{\epsilon - \Delta} \right) & -\epsilon < \omega < -\Delta \\ N_0 \left(\frac{\epsilon}{\epsilon - \Delta} \right) & \Delta < \omega < \epsilon \\ 0 & \text{otherwise} \end{cases} \quad (15)$$

$R(\omega)$ is modified in a straightforward way

$$R(\omega) = \begin{cases} 0 & \omega < 2\Delta \\ \tilde{\alpha}(\omega - 2\Delta) & 2\Delta < \omega < \epsilon + \Delta \\ \tilde{\alpha}(2\epsilon - \omega) & \epsilon + \Delta < \omega < 2\epsilon \end{cases} \quad (16)$$

where $\tilde{\alpha} = (\epsilon/\epsilon - \Delta)^2 \alpha$. (Fig. 1). This new form of $R(\omega)$ (imaginary part of the charge susceptibility) completely determines the revised lineshape through Eqn. 9.

On the other hand it is the change in the real susceptibility which leads to the shift in the XPS line. The real and imaginary parts of the density density correlation function are connected via Kramers-Kronig relations.

$$\chi'_\rho(\omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{d\tilde{\omega} \chi''_\rho(\tilde{\omega})}{\tilde{\omega} - \omega} \quad (17)$$

So the net line shift caused by the opening of the gap is given by:

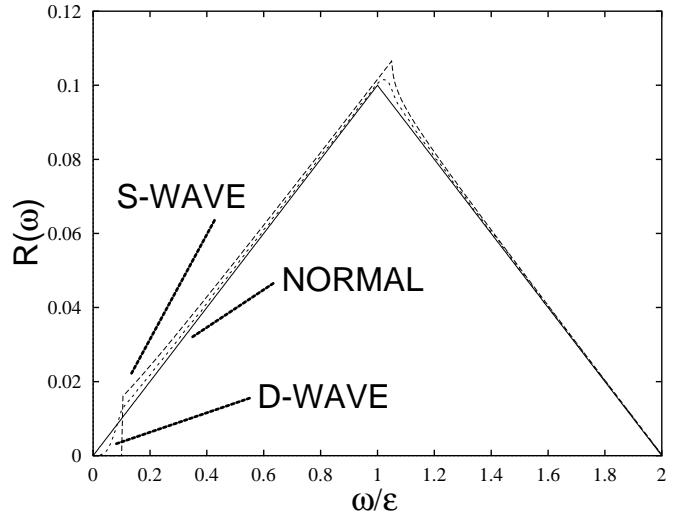


FIG. 4. $R(\omega)$ for a band metal in its normal state and for both s and d wave superconductors with a gap of $\Delta/\epsilon = 0.05$. ($\alpha = 0.1$)

$$\Delta E = \int_0^\infty d\tilde{\omega} \frac{R_N(\tilde{\omega}) - R_G(\tilde{\omega})}{\tilde{\omega}} \quad (18)$$

This is easily calculated for our model system.

$$\Delta E_{model} = \alpha \left\{ 2\epsilon \log 2 - \left(\frac{\epsilon}{\epsilon - \Delta} \right)^2 \left[2\epsilon \log \left(\frac{2\epsilon}{\epsilon + \Delta} \right) + 2\Delta \log \left(\frac{2\Delta}{\epsilon + \Delta} \right) \right] \right\} \quad (19)$$

We plot this shift as a function of gap in Fig. 3. It is a shift *away* from the power law tail, *i.e.* towards lower binding energy.

A plot of the modified spectral function, convoluted with a Lorentzian to mimic the finite core lifetime, is shown in Fig 2. While the coherent part of the spectral function (delta function) and its incoherent power law tail have been mixed by the convolution into one smooth lineshape, this clearly demonstrates both of the effects discussed above — there is an overall shift on the line towards lower binding energy (to the right), and spectral weight is transferred from the tail of the line to the peak, making it seem sharper and more symmetric. It is this sharpening of the line, observable provided that the charge gap (in this case 2Δ) is larger than the inverse of the core hole lifetime $1/\tau$, which is the key signature of the failure of the orthogonality catastrophe.

While this model is obviously a gross oversimplification, it does illustrate the two main effects of opening a gap at the fermi energy; to restate — the delta function peak at threshold is partially restored, and there is an overall shift in the position of the line shape towards lower binding energy.

IV. SUPERCONDUCTING SYSTEMS

A similar analysis can be performed for a superconductor. The same basic physics holds as for the toy model considered

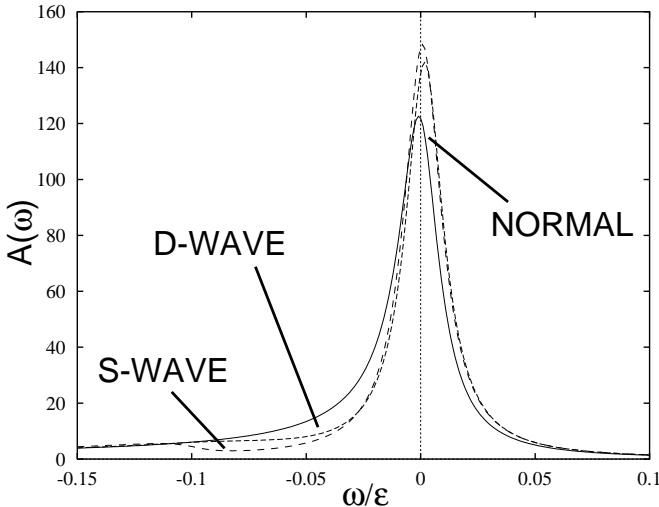


FIG. 5. XPS lineshapes for the normal metal and s and d wave superconductors with a gap of $\Delta/\epsilon = 0.05$. $1/\tau = 0.01\epsilon$ and $\alpha = 0.1$. As in the band metal, the superconductor lineshapes exhibit a delta function restoration and a overall shift upon the opening of the gap.

above, but the density-density correlation function now factorizes into normal and anomalous parts, so we must consider

$$P(i\Omega_n) = \frac{1}{\nu^2} \sum_{p,k} |V(k,p)|^2 \frac{1}{\beta} \sum_{ip_n} [\mathcal{G}(p, ip_n) \mathcal{G}(k, ip_n + i\Omega_n) - \mathcal{F}(p, ip_n) \mathcal{F}^\dagger(k, ip_n + i\Omega_n)] \quad (20)$$

where $i\Omega_n$ and ip_n are Matsubara frequencies.

Performing the frequency sum and continuing back to real frequencies yields the expression for $R(\omega)$ in a superconductor. At zero temperature, and for $\omega > 0$ this reduces to:

$$R(\omega) = \frac{1}{\nu^2} \sum_{k,p} |V(k,p)|^2 \times \{(v_p^2 u_k^2 + \frac{\Delta_p \Delta_k}{4E_p E_k}) \delta(\omega - E_p - E_k)\} \quad (21)$$

where $u_k^2 = \frac{1}{2}(1 + \frac{\xi_k}{E_k})$ and $v_k^2 = \frac{1}{2}(1 - \frac{\xi_k}{E_k})$ are the coherence factors and $E_k = \sqrt{\xi_k^2 + \Delta_k^2}$ is the excitation energy.

We now examine both s and d-wave superconductors for two different single particle energy dispersions, the linear dispersion of the previous section and a two dimensional tight binding model, and observe how the XPS lineshapes change upon the opening of the superconducting gap.

A. Linear Dispersion

As before, we assume a flat single particle density of states of the form:

$$N(\omega) = \begin{cases} N_0 & |\omega| < \epsilon \\ 0 & |\omega| > \epsilon \end{cases} \quad (22)$$

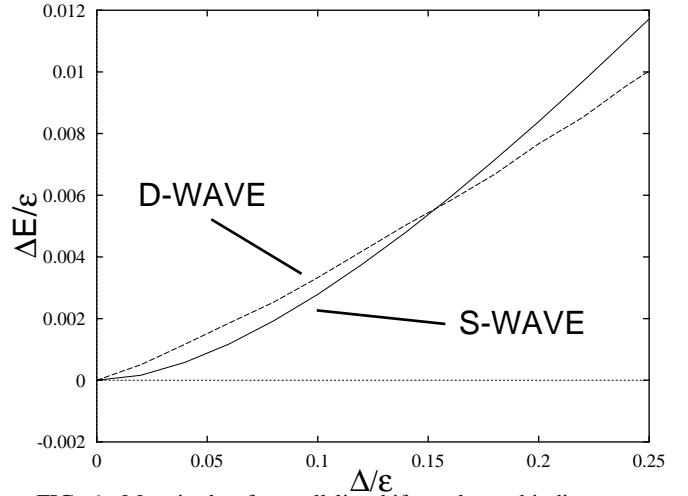


FIG. 6. Magnitude of overall lineshifts to lower binding energy for s- and d-wave superconductors assuming a linear single particle dispersion and asymmetry exponent $\alpha = 0.1$.

In a BCS s-wave superconductor with a spherical fermi surface in the normal state, the density of excitations is given by:

$$N(E) = \begin{cases} N_0 \frac{E}{\sqrt{E^2 - \Delta_0^2}} & \text{if } E > \Delta_0 \\ 0 & \text{otherwise} \end{cases} \quad (23)$$

Taking advantage of the delta function, an integral expression for the $R(\omega)$ of an s-wave superconductor is obtained.

$$R_S(\omega) = \alpha \int_{\Delta}^{\omega - \Delta} \frac{E_p(\omega - E_p) + \Delta^2}{\sqrt{E_p^2 - \Delta^2} \sqrt{(\omega - E_p)^2 - \Delta^2}} dE_p \quad (24)$$

We plot $R_S(\omega)$ in Fig. 4. The finite value of $R_S(\omega) = \pi\Delta$ at $\omega = 2\Delta$ is a consequence of the divergent, but integrable, density of states for $E \rightarrow \Delta$. In the same manner as before we can calculate the lineshape (Fig. 5) and shift (Fig. 6) for an s-wave superconductor. The existence of the gap in a superconductor produces the same effects as it does in the band metal. Again there is a partial restoration of the delta function peak, with a suppression of the powerlaw tail for $\omega < 2\Delta$, and an overall shift of the line. These effects are however somewhat less pronounced than in the toy model.

The case of a d-wave superconductor, where gap nodes lead to the presence of low energy excitations even for $\Delta \neq 0$, is subtly different. In this case the orthogonality catastrophe fails not because of the absence of zero energy excitations, but because the number of zero energy particle-hole pairs produced remains countable. More formally, the opening of a d-wave gap at zero temperature means that the leading term in $R(\omega)$ is no longer $\omega\Delta$ but $\beta\omega^3$, and so the logarithm found from Eqn. 9 in the case of a metal is eliminated. Unlike the s-wave case, the spectral function does have incoherent structure for $0 < \omega < 2\Delta$, but this is accompanied by a slightly

less pronounced transfer of spectral weight to a delta function at threshold.

The normal state has a circular fermi surface, the superconducting a two dimensional d-wave gap given by:

$$\Delta_D(\phi) = \Delta_0 \cos(2\phi) \quad (25)$$

with $0 \leq \phi \leq 2\pi$. Both $R(\omega)$ and the lineshift were obtained numerically via monte carlo integration. The lineshape was calculated as above.

The d-wave lineshape is shown along with that of the s-wave superconductor in Fig. 5 and the shift in Fig. 6. The presence of nodes in the gap leads to a slightly different gap dependence of the shift in the core line; in fact the d-wave line shift is *larger* at small Δ than in the s-wave case. The shifts can be fitted to power laws at small $\delta = \Delta/\epsilon$. The shift for the s-wave superconductor is given by $\Delta E_s = 1.11\alpha\delta^{1.60}$ and the d-wave shift by $\Delta E_d = 0.51\alpha\delta^{1.18}$ with an uncertainty of ± 0.01 in both the coefficient and the power.

If we assume that the gap opens as \sqrt{t} (where $t = (T_c - T)/T_c$), as would be expected of a meanfield order parameter for $T \approx T_c$, this translates into a shift in the line scaling as $\Delta E_s \sim t^{0.8}$ in the s- and $\Delta E_d \sim t^{0.25}$ in the d-wave case.

B. Tight Binding Model

In order to make closer contact with real HTc superconductors, we also evaluated lineshapes and shifts for a d-wave superconductor on a half-filled square lattice with underlying tight binding electron dispersion

$$\epsilon(k_x, k_y) = -2t(\cos k_x + \cos k_y) - 4t' \cos k_x \cos k_y \quad (26)$$

where t and t' is the nearest neighbour and t' the next nearest neighbour hopping integral. We chose $t'/t = -0.35$ as being representative of the in-plane Cu d band in a 'standard' 123 compound such as $YBa_2Cu_3O_{7-\delta}$. A 'standard' 2212 compound such as $Bi_2Sr_2CaCu_2O_{8+x}$ would have $t'/t = -0.2$ [15] but this will not change our results significantly.

We model a superconductor with d-wave symmetry on a square lattice with a gap function of the form

$$\Delta_d(k_x, k_y) = \frac{\Delta_0}{2}(\cos(k_x) - \cos(k_y)) \quad (27)$$

The results for $R(\omega)$ for this model of the normal and superconducting state are shown in Fig. 7. Once again we have set the coefficient of the leading linear term in the tight binding metal to be 0.1, so that the XPS asymmetry exponent for the system without gap is $\alpha = 0.1$. For comparison with our previous models we consider a gap size of $\Delta_0 = 0.05(4|t|)$. In general, t is of the order of 0.25meV . This gives $\Delta_0 = 50\text{meV}$ which is clearly larger than in the real compounds, but not unreasonably so; estimates for YBCO yield $\Delta_0 \approx 16\text{meV}$ and for BSSCO $\Delta_0 \approx 30\text{meV}$ [16].

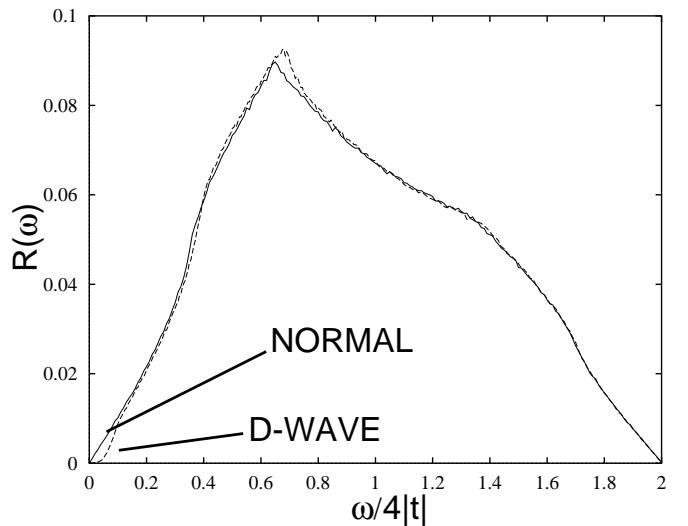


FIG. 7. $R(\omega)$ for tight binding metal with $t'/t = -0.35$ in the normal state and in a d-wave superconducting state with $\Delta_0/4|t| = 0.05$. Once again, $\alpha = 0.1$.

The resulting lineshapes and shifts for these coefficients are displayed in Figs. 8 and 9. Clearly the overall trends are exactly the same as found in the more general models; a sharpening of the XPS line and a shift to lower binding energy, but both trends are somewhat more marked than in the constant density of states model with the same parameters (*c.f.* Figs. 5 and 6), and the shift is now very nearly linear in Δ_0 .

The size of shift which we find must be something of an underestimate of the true shift in the cuprates, since we neglect all corrections to screening of the core hole which arise from electron-electron interaction, which is known to be strong in these systems. An improved estimate could be found by incorporating a Hubbard U term in the model, and evaluating an RPA series for the screened susceptibility. Such a procedure has been found to be necessary to obtain quantitative estimates of the local spin susceptibility in these systems [18]. Screening through electron-electron interaction is of course a dynamical process, and leads to corrections to the lineshape and gap dependence of the shift, as well as to its overall scale. These effects do *not* change the underlying physics, but can in principle be included in our calculation scheme, and may need to be included in any serious quantitative attempt to fit experimental lineshapes and shifts. We note also that attempts to fit the modified asymmetric lineshape found which we find in the presence of a gap with a standard Doniach-Sunjic lineshape can lead to artificially low values of α .

V. PSEUDOGAPS AND COMPARISON WITH EXPERIMENT

Pseudogap behaviour, which can be loosely defined as the (partial) loss of low energy excitations without the emergence of order, has been observed in many strongly correlated elec-

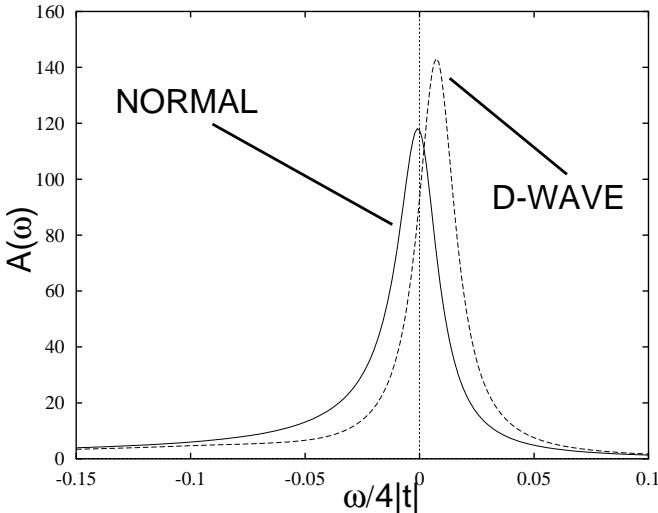


FIG. 8. XPS lineshapes for a tight binding metal in the normal state and in a d-wave superconducting state. $\Delta_0/4|t| = 0.05$, $1/\tau = 0.01|4t|$ and $\alpha = 0.1$.

tron systems [11]. The best known example is provided by the underdoped cuprate superconductors, where evidence for the opening of a pseudogap is found from NMR and ARPES experiments at temperatures between some high energy scale T^* and the superconducting transition temperature T_c . As a function of doping, T^* interpolates between the Néel temperature $T_N \sim 800K$ of the undoped Mott insulator and the transition temperature $T_c \sim 100K$ of the optimally doped superconductor.

What could XPS teach us about the opening of a pseudogap in this case? If the pseudogap seen in NMR is a precursor to the formation of superconducting order at low temperatures, coming about, for example, through the formation of “incoherent” pairs of electrons, then its effects on XPS lines will be broadly the same as those for a true gap. If on the other hand the pseudogap is not a precursor to superconductivity but, as has been suggested, a gap to spin excitations only, then XPS spectra would undergo little or no change at T^* . In this way the characteristic XPS signatures of gap opening — the sharpening of an asymmetric core line and/or a shift of lines to lower binding energy — could be used to distinguish between different theories of pseudogapped systems.

A shift in core lines to lower binding energy *has* been reported for XPS spectra taken above and below T_c , and for spectra taken above and below T^* in the cuprate high temperature superconductor $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ [17]. At first sight this seems to offer confirmation of exactly the type of effect which we predict on the basis of core hole screening. However, the quoted experimental values of the shift are of order 100meV for lines with an asymmetry $\alpha = 0.04$. This is much larger than can be reconciled with our simple model; using the tight binding model considered above, together with the parametrization $\alpha = 0.04$ and $\Delta_0 = 30meV$, we would anticipate a shift in the XPS line of order 1.2meV.

Of course, analyzing the metal superconductor transition in

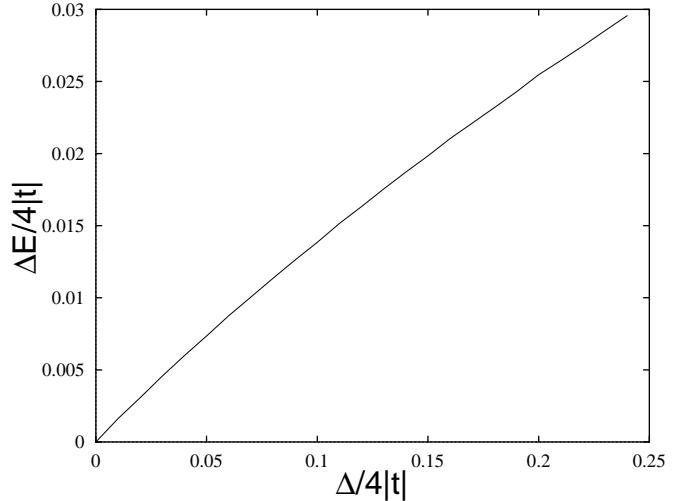


FIG. 9. Overall line shifts to lower binding energy for a d-wave superconductor with a tight binding dispersion in the normal state as a function of the gap parameter $\Delta_0/4|t|$, once again $\alpha = 0.1$.

$Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ in terms of tight binding model and BCS models will not always give reliable answers, especially in the underdoped “pseudogap” regime. Nevertheless we believe our calculation provides the correct starting point for understanding such experiments, and mechanisms other than the suppression of screening of the core hole by the opening of the gap should therefore also be considered.

VI. CONCLUSIONS

The gross effects seen in XPS lineshapes for metallic systems when a gap opens are very robust and independent of the choice of model. The core line undergoes an overall shift to lower binding energy and spectral weight is transferred from the powerlaw tail of the line to its peak, leading to a sharpening of the line and some loss of overall asymmetry. Modifications to lineshape are more easily seen in systems where the gap is large compared with the intrinsic width of the core level. In this limit subtle differences can be also seen between different models.

The shift in core lines shows power law dependence on the size of the gap, with different power laws for superconductors with s- and d-wave gap symmetries and for a tight binding model as compared with a model with a constant density of states. In principle XPS offers a means of distinguishing between different gap symmetries in systems with complicated order parameters.

Where sufficiently narrow core lines can be found, XPS offers a potentially rich source of information about the changes which take place in many electron systems when a gap opens, and might be particularly useful if taken in parallel with NMR measurements. The opening of pseudogaps could also be studied from the perspective of XPS measurements.

For simplicity, we have chosen to work within perturbation theory and to discuss only models which have simple non-interacting quasi-particle excitations. Both of these restrictions can be relaxed, and many of the same physical considerations apply to core levels coupled to strongly interacting electron systems. Experimentally it might well be interesting to look at the effect on XPS lines of metal-insulator or charge density wave transitions where the intrinsic gap scale is very much larger, and the effects of gap opening can be expected to be more pronounced.

Acknowledgments. It is our pleasure to acknowledge many helpful conversations with Jim Allen, Franz Himpsel, and Robert Joynt. This work was supported under the grant DMR-9704972 .

- [1] T. Imai *et. al.* Phys. Rev. Lett. **70**, 1002 (1993).
- [2] N. Shannon and R. Joynt, *Preprint* cond-mat/9806169.
- [3] N. Shannon, *Preprint* cond-mat/0003385.
- [4] N. Shannon, *Preprint* cond-mat/9910121.
- [5] S. Doniach and M. Sunjic, J. Phys. C **3**, 285 (1970).
- [6] G. K. Wertheim and P. H. Citrin, in *Photoemission in Solids I* (Springer, Berlin 1978).
- [7] M. Combescot and P. Nozieres , J. Physique **32** , 913 (1971).
- [8] G. D. Mahan, in *Many Particle Physics*, (Plenum, New York, 1990), pp 178.
- [9] D. C. Langreth, Phys. Rev. B **1**, 471 (1972).
- [10] P. W. Anderson, Phys. Rev. Lett. **18**, 1049 (1967).
- [11] This rule of thumb leads to some confusion of terms in cases where a true gap opens in the absence of long range order, for example in the one-dimensional Hubbard model at half filling.
- [12] J. J. Hopfield, Comments on Solid State Physics **II**, 40 (1969). See also J. J. Hopfield in *Proceedings of the International conference on the Physics of Semiconductors, Exeter, 1962* (The Institute of Physics and the Physical Society, London, 1962), pp 75.
- [13] K. Ohtaka and Y. Tanabe Rev. Mod. Phys. **62**, 929 (1990). For a recent pedagogical overview see also A. Gogolin, A. Nersesyan and A. Tsvelik, *Bosonization of Strongly Correlated Electron Systems* (Cambridge, UK. 1998).
- [14] P. Noziéres and C. T. de Dominicis, Phys. Rev. **178** 1097 (1969).
- [15] B. Koltenbah and R. Joynt, Reports on Progress in Physics **60**, 23 (1997).
- [16] Z. X. Shen and D. S. Dessau, Phys. Repts. **253**, 1 (1995).
- [17] O. Tjernberg *et. al.* , Phys. Rev. Lett. **79**, 499 (1997).
- [18] R. Joynt and Q. P. Li, Phys. Rev. B **47**, 530 (1992)